



# Large scale smelting of speiss and arsenical copper at Early Bronze Age Arisman, Iran

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## ARTICLE INFO

### Article history:

Received 6 May 2011

Received in revised form

7 January 2012

Accepted 10 January 2012

### Keywords:

Arsenic

Copper

Smelting

Alloy

Early Bronze Age

Iran

Arisman

## ABSTRACT

We report analyses of different slag types found at the Early Bronze Age site of Arisman in North-West Iran. Here, an estimated 20 tons of slag provide evidence of sustained and large-scale production of metal, using both furnaces and crucibles. The results show that both speiss, an iron-arsenic alloy, and arsenical copper were produced, apparently side-by-side at the same site but using different ores and processes. We offer a tentative outline of the metallurgical processes involved in the production of these arsenic alloys and an explanation why speiss needed to be produced from arsenopyrite in a separate step, instead of using the mineral in its native form as a source for arsenic. We suggest that the speiss was then added either to secondary copper ore or to separately smelted copper metal, in order finally to produce arsenical copper in a regular and well-controlled process.

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## 1. Introduction

Arsenical copper is an important alloy in the development of copper metallurgy, typically occurring in a relatively short-lived transition period between the uses of unalloyed copper and tin bronze (Charles, 1967). This pattern has been documented for such diverse regions as the Iberian Peninsula, the Balkans, the British Isles, Siberia, Central Asia, and South America. In the Old World, Iran is exceptional in its long-lasting preference for arsenical copper at a time when most surrounding regions had already switched to tin bronze (Heskel and Lamberg-Karlovsky, 1980; Heskel, 1983; Pigott, 1999; Thornton, 2009). This makes Iran an ideal region to investigate the production of arsenical copper in more detail. Previous research has shown that a number of different routes could lead to arsenical copper, including the smelting of complex sulph-arsenide ores (fahlore, etc.) (Rostoker et al., 1989; Rostoker and Dvorak, 1991; Lechtman, 1996; Lechtman and Klein, 1999; Höppner et al., 2005), the smelting of native copper and copper-arsenide minerals (Budd et al., 1992), and the conscious addition of an arsenic-rich mineral such as realgar or orpiment, arsenopyrite or löllingite to copper metal or copper ore (Heskel, 1983; Moorey, 1999; Thornton et al., 2002; Pigott, 2008).

More recently, Thornton et al. (2009) proposed that an artificial iron-arsenic alloy, called speiss, was produced in Early Bronze Age Tepe Hissar, North Iran, presumably to be added to copper metal for the production of arsenical copper. Even though finds of speiss are relatively well-known from several EBA copper workshops, suggesting that this material was widely used and traded (see Rehren et al., 1988; Keesmann and Moreno-Onorato, 1999; Hauptmann et al., 2003; Müller et al., 2004; Doonan et al., 2007), the Tepe Hissar study was based on only a small number of finds from an urban workshop – hardly enough to postulate with confidence a regular, intentional speiss production. Indeed, modern conventional metallurgical wisdom has it that the production of speiss has to be avoided at almost all cost, since it is more harmful than useful for any practical purpose (R. Maddin personal communication, 2009).

It is therefore of considerable importance that recent excavations by the German Archaeological Institute at the EBA metallurgical site of Arisman in Western Iran (Fig. 1) have uncovered large quantities of slag derived from the routine production of speiss as a material in its own right – in the context of arsenical copper production, but in an independent smelting operation leaving behind slag in the order of several tons.

First discovered in 1996 by a local resident, the site of Arisman has undergone four seasons of excavations between 2000 and 2004 by a joint Iranian-German team consisting of the Iranian Cultural

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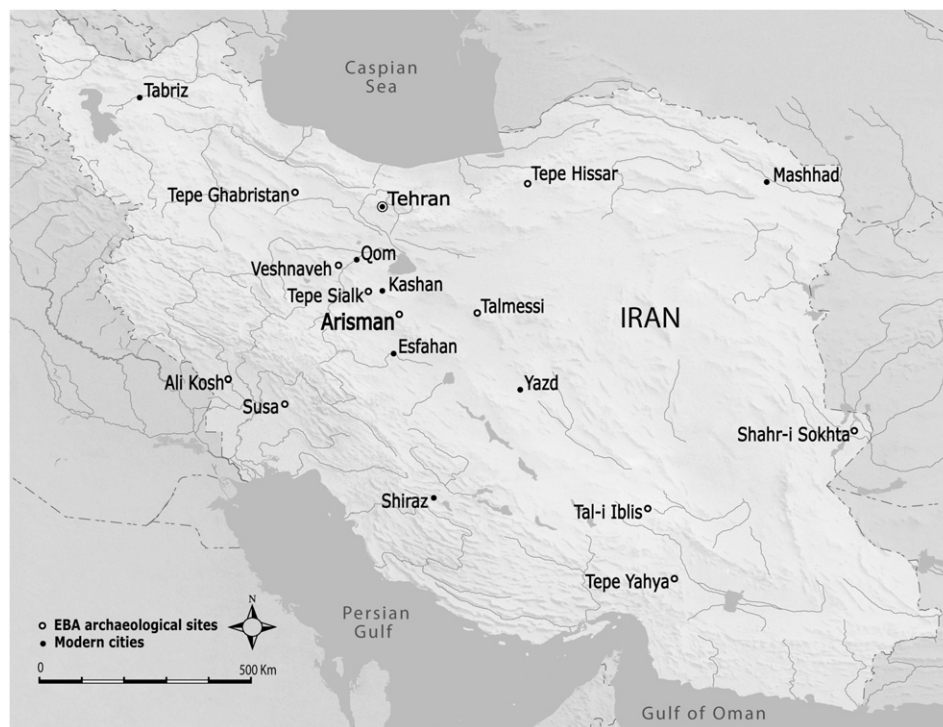


Fig. 1. Map of Iran with EBA archaeometallurgical sites.

Heritage Organisation (ICHO), the Geological Survey of Iran (GSI), the German Archaeological Institute (DAI), the German Mining Museum in Bochum (DBM) and the Institute of Archaeometry of the University of Technology Bergakademie Freiberg (Chegini et al., 2000, 2004; Vatandoust et al., 2011). Ceramic typologies associate Arisman chronologically with the Sialk III 6–7, Sialk IV, and Ghabristan IV periods, dating it from the later fifth/early fourth millennium BC to the middle of the third millennium BC (Helwing, 2008). Situated ca. 1000 m above sea level in the transitional zone between the north-eastern slopes of the Karkas Mountains and the lower plains of the Iranian Plateau (Fig. 1), the site of Arisman is located just 60 km from the well studied EBA metallurgical site of Tepe Sialk.

Excavations focused on a number of low settlement mounds that revealed distinct activities and occupations. The earliest occupation of the site, dating to the Sialk III 6 and 7b periods, is

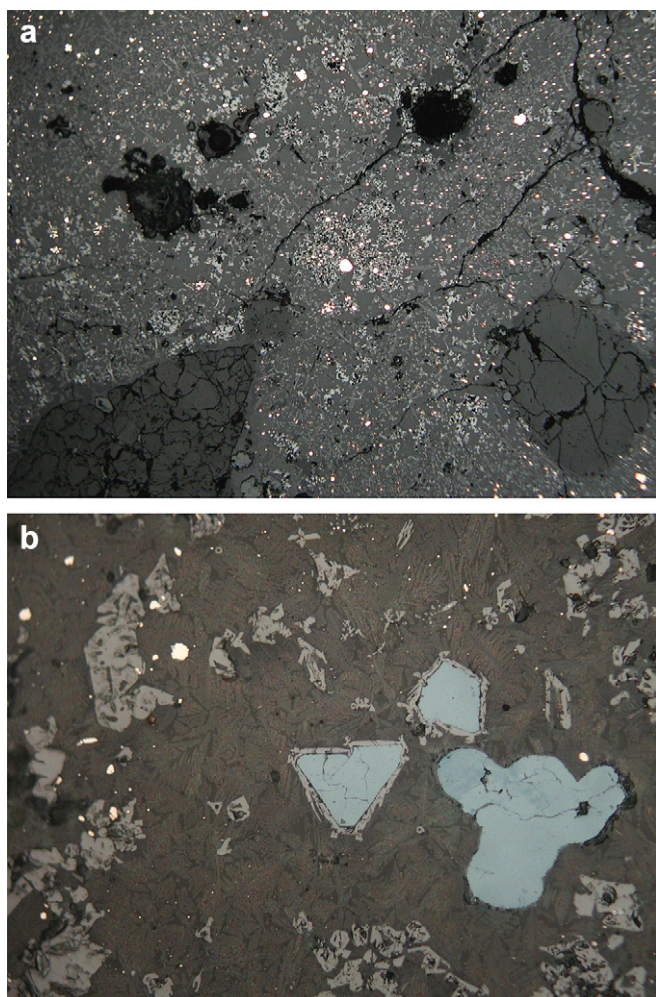
believed to be representative of domestic scale, crucible bound smelting of the late Chalcolithic to EBA. Over the course of the next several centuries, metallurgical activities appear to have intensified but also shifted geographically to several other areas of the site, culminating in the formation of a large slag heap containing an estimated 20 tons of slag in area A.

Radiocarbon dated to between 3100 and 2900 BC (Görsdorf, 2011), this slag heap corresponds well with associated ceramics tied to the Sialk IV period of the EBA. The mound consists of a series of layers of sand and slag 10–40 cm thick, with at least four major deposition events separated by thin lenses of sand (see Fig. 3 in Steiniger, 2011: 70). In addition, there are numerous micro-depositional layers in the centre of the heap associated with a mudbrick platform and furnace structure that showed signs of having been rebuilt dozens of times. Excavations revealed the slag heaps to be composed in about equal parts of grey copper rich slags



Fig. 2. Left – slag heap A section with furnace in the bottom. Right – plan and section of stage 5c of the furnace. From Steiniger (2011: 74–76).





**Fig. 3.** a Micrograph of typical texture of 'grey' copper slag with copper prills and magnetite clusters in the centre of the image and a mixture of magnetite spinels, large melilite crystals, wüstite dendrites, and arsenical copper prills elsewhere, and residual quartz grains in the lower right and left corner. Sample FG-030114, width of image c 1.5 mm. b Micrograph of typical texture of 'grey' copper slag with copper matte (blueish, centre and right) surrounded by magnetite, and magnetite clusters, melilite, wüstite, and arsenical copper prills elsewhere. Sample FG-000115, width of image c 0.3 mm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

with green stains and brown slags with no copper staining, and smaller amounts of black glassy slag. It is important to note that there was no visible stratification in the slag heap, neither vertically nor horizontally, i.e. grey and brown slags were completely mixed. The chemical and metallurgical analysis of these slags was undertaken at UCL as part of an MSc thesis specifically aimed at the brown slags and their potential relation to speiss production (Boscher, 2010), building on initial results from a larger analytical programme based at the University of Tübingen covering the whole of the metallurgical evidence present at Arisman (Pernicka et al., 2011). Our results presented here demonstrate the existence of two separate formation processes, one of which had for intended output ferrous speiss. We argue that this was then to be used in the production of arsenical copper.

## 2. Materials and methods

Analysis on 11 samples selected from c 10 kg of slags from within Arisman's slag heap A was undertaken at the Wolfson Archaeological Science Laboratories at the UCL Institute of

Archaeology. The material is part of a larger sample of metallurgical debris currently held in Mannheim, from which a set of lead isotope analyses and a preliminary set of X-ray fluorescence analyses exist (Pernicka et al., 2011). Approximately half of the samples studied here were grey copper rich slags while the other half consisted of brown slags. They were visually distinguishable by their colour, the presence of green corroded prills in the grey slags only, and higher porosity and more 'rusty' appearance of the brown slags; both types were often associated with fragments of technical ceramics. The black glassy slag is subject of a current separate study, and will not be considered here.

The assemblage was sampled judgmentally in order to obtain as broad a sample as possible. In cases where a fragment was of particular interest, multiple samples were taken of the same piece. A total of fourteen resin blocks were prepared from eleven different pieces of slag. Seven specimens were taken from five grey slags, and seven specimens from six brown slags.

Following a macroscopic assessment of the total assemblage, samples were cut and mounted in resin before being polished down to 0.25  $\mu\text{m}$ . Prepared samples were analysed using reflected light optical microscopy with a Leica DMLM optical microscope in plane polarized light in order to determine the samples' crystalline phases, colour, homogeneity, porosity, and inclusions. Cross polarized light was also used to help identify internal microstructures and phases as well as characterise the technical ceramic fabrics.

The samples were then analysed using a Philips XL30 Scanning Electron Microscope with an Oxford Instruments EDS attachment using INCA software in order to obtain a quantitative understanding of the chemical and crystallographic composition of the assemblage. The EDS was set up at an accelerating voltage of 20 kV, a spot size of 5.1, a working distance of 10 mm, and an operating dead time between 30 and 40%. Slag analyses are reported as averages of several measurements done at low magnification, typically analysing areas of c 2.4 by 1.8 mm, and avoiding residual quartz inclusions or major metal and matte prills. The instrument's beam current stability was verified approximately every 30 min using a cobalt standard and kept within reasonable range to avoid too large normalisation factors when normalising results to 100 weight percent. A ZAF correction procedure was used to calculate chemical compositions from the measured intensities of characteristic energy lines. Several certified reference materials were analysed to monitor adequate quantitative reliability; for oxide compositions, we believe our results to be correct within ten percent relative of the measured value for concentrations above c. five weight percent. In contrast, our analyses of BCR 691 Alloy C, arsenical copper with certified 4.6 wt% As, differed more than 40 percent relative to the certified value, typically reporting between 6.1 and 7.1 percent As. However, these alloys were developed for use with XRF analysis and not for microbeam analysis, and Constantinides et al. (2001) reported major chemical heterogeneities for this set of alloys, including the presence of numerous sulphide and oxide inclusions in the arsenical copper alloy. Future work will focus on the reliable quantitative analysis of arsenical copper prills using microbeam analysis; for the time being we use the arsenic values of our analyses as reported by the SEM–EDS software. All results were normalized to 100% in order to facilitate comparison despite the varying electron beam intensity, and reported either as oxides with oxygen calculated by stoichiometry for materials such as the ceramic fabric and slag matrix, or as elemental weight percentages for the metallic prills.

## 3. Results

Visual inspection during excavation had identified several different types of metallurgical debris among the c. 20 tons of the

**Table 1**

Bulk chemical composition of grey slag matrix by SEM–EDS area analysis. Data in wt%, normalised to 100.

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	FeO	CuO	As <sub>2</sub> O <sub>3</sub>
FG-030121	0.9	1.6	5.3	45	0.1	0.0	1.6	8	0.0	0.0	37	1.0	0.0
FG-030120	1.2	2.2	9.6	47	0.0	0.3	2.6	14	0.4	0.2	20	2.6	0.0
FG-000115	1.8	2.6	8.5	40	0.0	0.1	1.9	13	0.3	0.0	29	2.9	0.1
FG-000119	1.1	2.5	8.4	40	0.6	0.3	1.3	15	0.2	2.4	27	1.0	0.1
FG-030114	2.5	2.3	8.2	43	0.0	0.3	2.3	14	0.4	0.5	24	2.4	0.3
Mean	1.5	2.2	8.0	43	0.1	0.2	1.9	13	0.3	0.6	27	2.0	0.1

slag heap in area A of Arisman I (Fig. 2). Among these are significant amounts of technical ceramics, including the nearly complete furnace which had been covered by subsequent slag layers, and numerous crucible fragments (Chegini et al., 2000); grey slag with green staining; brown slag with rusty corrosion colours; and black, glassy slag. The majority of material consists of grey and brown slag, present in roughly equal quantities. This paper focuses on these two slag types; for a more comprehensive presentation of the material found at Arisman A, see Pernicka et al. (2011).

### 3.1. The grey slag

Grey slags can be described macroscopically as dense, relatively homogeneous, with green copper oxide staining on the outer surface, and sometimes showing flow patterns typical of tapped slags. When studied microscopically, they were found to have large, incompletely reacted fragments of gangue material, typically quartz, as well as large quantities of matte (5 µm–15 mm in size) and arsenical copper metal prills (5–20 µm in size). Only one of the five samples (FG-030120) contained no copper sulphide. SEM–EDS bulk area analysis, avoiding the residual quartz inclusions and major prills (Table 1), showed that the slag matrices were mainly composed of SiO<sub>2</sub> and FeO, but also had significant amounts of CaO and Al<sub>2</sub>O<sub>3</sub>, allowing the formation of a number of crystal phases in the melilite (general formula (CaNa)<sub>2</sub>(AlMgFe<sup>2+</sup>)<sub>2</sub>[(AlSi)SiO<sub>7</sub>]) and pyroxene (general formula Me<sup>2+</sup>Me<sup>3+</sup>(Si,Al)<sub>2</sub>O<sub>6</sub>) groups. Magnetite-rich spinels (mainly Fe<sub>3</sub>O<sub>4</sub>) could also be seen in every grey slag sample, often in large amounts and forming distinct clusters rich in copper metal. Wüstite dendrites ('FeO') were observed in three of them, suggesting more reducing atmospheric conditions present in some smelts. The two wüstite-free samples both contained olivine crystal lathes and one of them also contained fayalite crystal chains. It should be noted that the bulk composition of these grey slags invariably contained significant quantities of copper (2.0 wt%) and very little arsenic (0.1 wt%). Spot analysis by SEM–EDS (Table 2) showed that while all the grey slag samples were dominated by arsenical copper prills, two samples also contained relatively pure copper prills. These copper prills tended to have much lower iron content (c 1 wt% Fe) than the arsenical copper prills, which had on average 3.1 wt% Fe.

**Table 2**

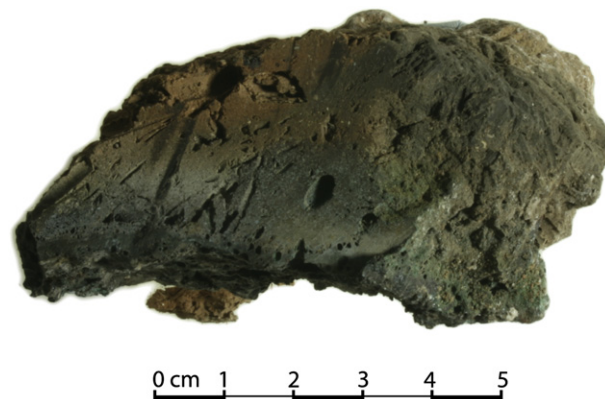
SEM–EDS spot analyses of grey slag metal prills; "bdl" means "below detection limit".

	O	S	Fe	Cu	As	Sb	Ni
<i>Arsenical copper prills</i>							
FG-030121	0.5	0.7	4.2	92	3.0	bdl	bdl
FG-030120	0.9	bdl	2.1	93	4.5	bdl	bdl
FG-000115	0.5	bdl	2.8	92	2.6	1.7	bdl
FG-000119	0.8	bdl	3.3	87	7.7	bdl	0.6
FG-030114	0.6	bdl	2.9	92	3.8	bdl	bdl
Mean	0.7	N/A	3.1	91	4.3	N/A	N/A
<i>Pure copper prills</i>							
FG-030120	0.6	bdl	1.7	98	0.1	bdl	bdl
FG-000119	0.6	bdl	0.4	98	0.1	bdl	0.1
Mean	0.6	bdl	1.0	98	0.1	bdl	N/A

Bulk chemical composition of numerous samples from the same slag heap has also been determined by Pernicka et al. (2011) using XRF, and been found to be consistent with the data found for the samples analysed in this study. The only significant differences are lower SiO<sub>2</sub> and FeO contents (32.3 wt% and 24.7 wt% respectively on average) and elevated CaO and CuO contents (16.9 wt% and 10.4 wt% respectively) in the XRF analyses, the latter probably reflecting the indiscriminate analysis of slag matrix and metal inclusions.

A number of grey slags had associated technical ceramics. These ceramics tended to be highly porous with clear evidence of long thin grass-like organic temper (approximately 1 mm by 5 mm in size) (Fig. 4). They were highly degraded and crumbly and on occasion embedded within the slag; clearly the poorly fired remains of furnaces much like the one uncovered within the slag heap. They were generally reddish orange on the outside and light grey on the inside, which would suggest that a reducing atmosphere was present within the furnaces during firing. Bulk chemical composition was obtained for one sample using SEM–EDS area analysis and is presented in Table 3.

The data clearly show that the grey slag resulted from the smelting of a copper ore, producing arsenical copper. It is noteworthy that the slag is not very well fused, with numerous inclusions of rock fragments, and differences in melt phase composition both between and within single specimens. Clearly, this was very much a pasty and incompletely reacted material, and not the fluid tap slag of later periods. The presence of sulphide inclusions demonstrates that the charge contained considerable amounts of sulphur, while the overall ratio of matte inclusions to metal prills, and the relatively low iron oxide content of the slag, suggest that the ore was probably oxidic, and not sulphidic such as chalcopyrite. Several instances were found where copper prills in and around gangue inclusions were free of arsenic and low in iron (Fig. 5), while in the same sample prills further away and deep in the melt phase were iron-rich arsenical copper (4.5 wt% arsenic). Overall, the conditions here appear to have been rather strongly reducing,

**Fig. 4.** Photograph of typical copper slag furnace ceramic, showing organic temper voids.



**Table 3**

Bulk chemical composition of grey slag ceramic by SEM–EDS area analysis. Data in wt%, normalised to 100.

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	FeO	CuO	As <sub>2</sub> O <sub>3</sub>
FG-030116B	2.3	2.9	13	54	0.3	0.4	2.7	18	0.5	5.9	0.1	0.4

indicated by the iron content of the copper metal and the occurrence in some cases of wüstite dendrites, while the operating temperatures were probably just high enough to produce a semi-liquid slag.

### 3.2. The brown slag

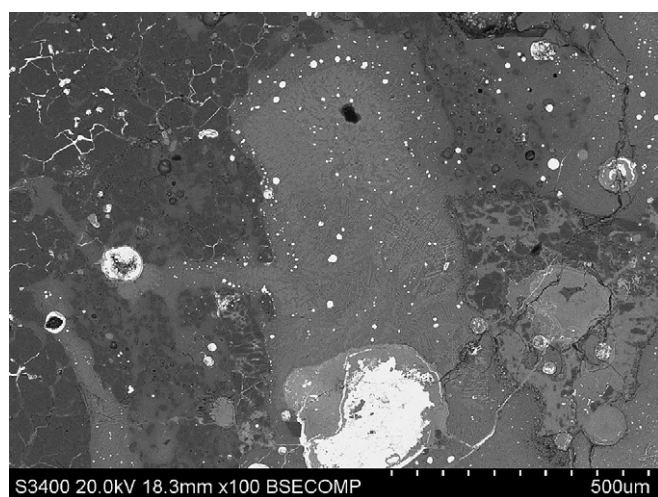
Visual examination of the brown slags showed that they tended to be much more porous and heterogeneous than their grey counterparts, with large gangue inclusions and corrosion-induced iron oxide staining. Much like the grey slags, these sometimes showed clear evidence of tapping. In at least one case, it was found that the slag had been poured onto a flat piece of ceramic resting directly on the ground surface and that the slag had been scraped to the side, likely a fragment of the tapping crucibles described by Steiniger (2011: 76–77). Microscopically, these slags had crystalline structures that, much like the grey slags, fell in the melilite and pyroxene systems, but with the addition of some olivine group crystals (general formula  $\text{Me}_2^{2+}\text{SiO}_4$ ). Magnetite-rich spinels could be seen in all the brown slag samples, and in some cases long skeletal chains of kirschsteinite ( $\text{CaFeSiO}_4$ ) or hedenbergite ( $\text{CaFeSi}_2\text{O}_6$ ) could be observed. Significantly, these brown slags were dominated by ferrous speiss prills ranging in size between 5  $\mu\text{m}$  and 2 mm. Bulk chemical composition was determined by SEM–EDS area analysis (Table 4) and confirmed a CaO rich slag mainly composed of SiO<sub>2</sub> and FeO. It was found that, in clear contrast to the grey slags, these samples had relatively high bulk arsenic content (1.6 wt%) with copper concentrations below the SEM–EDS detection limit (estimated at 0.1 wt%). These results compare very well with the bulk XRF analyses performed by Pernicka et al. (2011), with the only notable difference being the lower SiO<sub>2</sub> (35.5 wt%) content and the higher CaO (20.9 wt%) content within the XRF data.

Spot analysis of the speiss prills (Table 5) showed the presence of various phases within them. The smallest ones were typically

composed of a single phase of FeAs, although in some cases prills composed of a single FeAs<sub>2</sub> phase were also present. Larger speiss prills on the other hand were usually composed of two phases. In most cases, these larger prills had eutectic structures consisting of FeAs and an almost entirely corroded phase interpreted as having been Fe<sub>2</sub>As (Fig. 6), based on evidence from less corroded areas. Present in a single, highly vitrified sample, were prills consisting of angular grains of FeAs with an arsenic enriched phase of FeAs<sub>2</sub> present at the grain boundaries (Fig. 7). According to Raghavan's (1988) study of the Fe–As system, all of these speiss structures are formed between 825 °C and 1000 °C, with the different phases forming dependent on the arsenic to iron ratios and atmospheric conditions within the furnace.

A number of fragments of brown slags were attached to the remains of technical ceramics. However, in this case, it was possible to distinguish two different types of ceramics based on macroscopic evidence. The first type of ceramic can be described as largely porous, reddish brown, tempered with organic material and typically in hot contact with the slag, suggesting that these were part of the furnace structure. The other type can be described as much denser, lacking in organic temper, very flat, and with little if any interaction with the slag. This 'cold' contact is believed to be part of a tapping surface or receptacle and fits in well with other finds at the site (Steiniger, 2011: 76). Bulk chemical analysis using SEM–EDS (Table 6) showed that both types were essentially identical chemically. It is clear that both types were produced using the same raw materials but that organic temper was added only to the furnace ceramic, most likely in order to enhance insulating properties of the furnace walls. The tapping surfaces and receptacle were likely fired in a kiln where conditions were much easier to control, and organic tempering was undesirable since a smooth surface was to be achieved.

The brown slag is very similar in its silicate basis to the grey slag reported above; the main difference is in its slightly lower iron oxide content and somewhat elevated lime content. Thus, we may assume that a similar type of gangue and furnace wall contribution formed this slag. However, significant differences also exist between the two slags; the brown slag has hardly any copper, but an about tenfold higher average arsenic oxide content (Fig. 8). Almost all metallic inclusions in the brown slag are iron–arsenic compounds, with rare sulphides. This, and the virtual absence of copper from these slags, matches the earlier observation by Thornton et al. (2009) from Tepe Hissar, and is a defining feature of speiss slag, that is slag from a smelting operation aimed at producing speiss. The furnace atmosphere here appears to have been more oxidising than in the case of the green copper



**Fig. 5.** SEM-BSE image of incompletely reacted gangue material (dark, left and upper left and upper right corner) surrounded by pure copper prills (bright, round). Copper-rich phases, probably from corrosion, fill also cracks and voids (upper left corner and centre bottom). Light grey area in the centre is slag. Sample FG-030120.

**Table 4**

Bulk chemical composition of brown slag matrix by SEM–EDS area analysis. CuO content was below detection limit of 0.1 wt% in all samples. Data in wt%, normalised to 100.

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	FeO	As <sub>2</sub> O <sub>3</sub>
FG-030116A	2.2	1.2	9.2	44	2.4	14	0.4	1.0	24	1.2
FG-030117	2.3	1.8	8.5	40	1.6	15	bdl	0.9	29	1.4
FG-030119A	1.9	2.3	10.5	48	2.5	16	0.5	1.1	16	1.1
FG-030119B	2.3	1.5	7.8	39	1.6	19	bdl	1.2	24	3.4
FG-040919	2.1	1.8	9.2	43	2.2	19	0.6	0.5	20	0.8
FG-040919B	2.0	1.6	8.0	36	1.8	15	0.4	bdl	34	1.6
MEAN	2.1	1.7	8.9	42	2.0	16	0.3	0.9	24	1.6

**Table 5**

SEM–EDS spot analyses of brown slag speiss prills, in wt%, normalised to 100.

	O	S	Fe	Cu	As
FG-030116A	0.6	1.2	44	bdl	54
FG-030117	1.9	0.9	42	0.2	54
FG-030119A	bdl	2.7	41	0.4	56
FG-030119B	6.4	1.9	42	bdl	48
FG-040919	1.3	2.1	44	bdl	52
FG-040919B	3.9	1.1	45	bdl	49
Mean	2.3	1.6	43	0.1	52

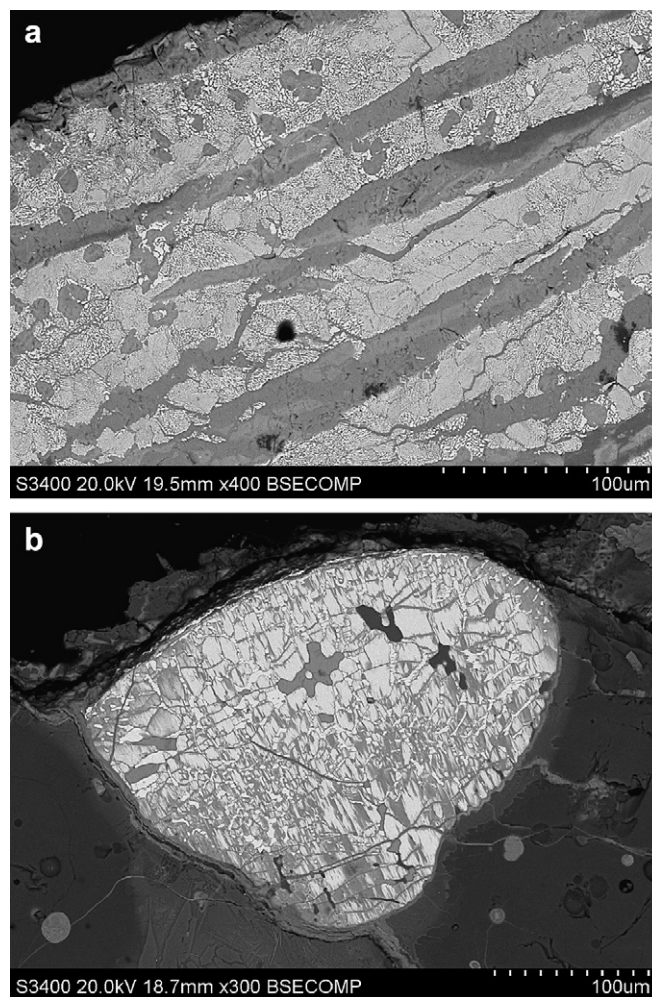
slag – several of the speiss inclusions show signs of hot oxidation, and any free iron oxide phases are invariably magnetite, not wüstite. The operating temperature appears to have been lower than for the copper slag, as indicated by the higher porosity.

#### 4. Discussion

The presence of large quantities of copper slag and speiss slag closely mixed in the same slag heap, with few if any transitional pieces, suggests that these were formed from two separate smelting operations going on in parallel, probably in very close proximity, and over some considerable period of time. It is also clear that both operations were done routinely and intentionally, and were not haphazard attempts to smelt variable or mixed ores. The production of large quantities of arsenical copper does not surprise at this time and place; however, evidence for the smelting of speiss on such a scale is unprecedented in the literature, and needs further discussion. What are the reasons for producing speiss in the first place, and not using the arsenic-rich ore mineral as it is? Would co-smelting copper ore and arsenic ore in a single operation not be more economical, particularly regarding fuel consumption in a landscape that was presumably already heavily exploited for wood?

##### 4.1. Smelting speiss

The evidence from the brown slag shows beyond reasonable doubt that it originates from the production of an iron–arsenic alloy, of an estimated composition near FeAs; prills trapped in the slag range from Fe<sub>2</sub>As to FeAs<sub>2</sub>. The absence of base metals from these



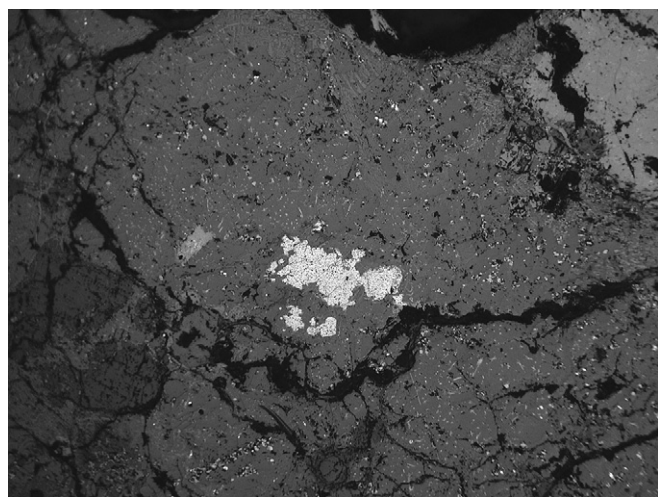
**Fig. 7.** a SEM–EDS image of a large speiss prill. The bright phase is FeAs while the corroded dark phase is presumed to have been Fe<sub>2</sub>As. Sample FG-030119A. b SEM–EDS image of a large speiss prill. The mid grey grains are FeAs while the slightly brighter phase at the grain boundaries is FeAs<sub>2</sub>. Dark grey are corrosion products. Sample FG-030119B.

slags above levels of a small fraction of a percent rules out that the speiss formed during lead or copper smelting – operations usually associated with the formation of speiss as an unwanted waste product (Craddock, 1995; Kassianidou, 1998; Keesmann, 1999; Rehren et al., 1999). Theoretically, the slag could originate from smelting iron arsenates such as scorodite, commonly formed during weathering of arsenopyrite. This would be consistent with the regular presence of magnetite in these slags, as the redox conditions necessary to produce ferrous speiss from such fully oxidised minerals span the stability fields of both magnetite and wüstite (Fig. 9). However, the large quantities of brown slag present and the relative rarity of massive occurrences of scorodite

**Table 6**

Bulk chemical composition of brown slag ceramics by SEM–EDS area analysis. Data in wt%, normalised to 100.

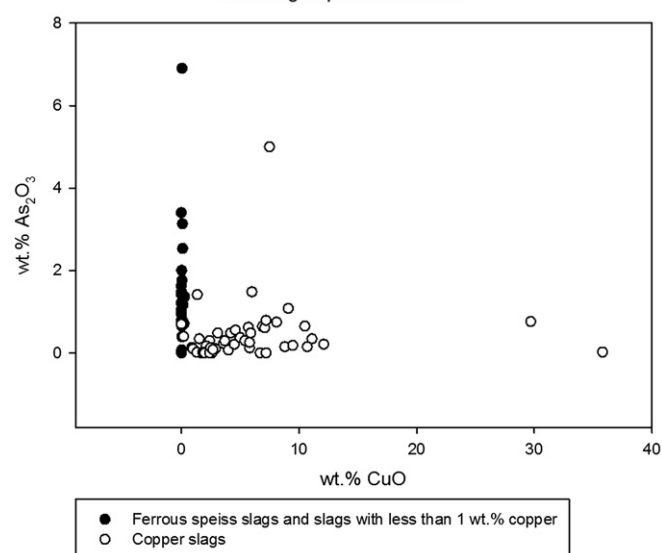
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	FeO	As <sub>2</sub> O <sub>3</sub>
FG-030117	1.7	3.1	12	56	bdl	2.6	19	bdl	5.2	0.7
FG-030119A	1.5	3.4	12	46	7.8	2.2	19	0.4	5.3	1.0
FG-030119B	2.9	3.9	15	54	bdl	1.3	14	0.8	7.4	0.7
FG-040919B	2.0	3.6	14	57	bdl	3.6	12	0.7	6.2	0.4
Mean	2.0	3.5	13	53	2.0	2.4	16	0.5	6.0	0.7



**Fig. 6.** Micrograph of typical texture of 'brown' speiss slag with speiss prills (bright, centre) surrounded by slag with melilite and minor amounts of magnetite (small medium grey crystals) in glassy matrix, and residual quartz grains (dark, centre left). Sample FG-000115, width of image c 0.3 mm.



Arsenic and Copper content in copper smelting and speiss smelting slags  
Including unpublished data



**Fig. 8.** Scatterplot of the arsenic and copper content present in the two types of slags analysed for this study along with the data from Pernicka et al. (2011).

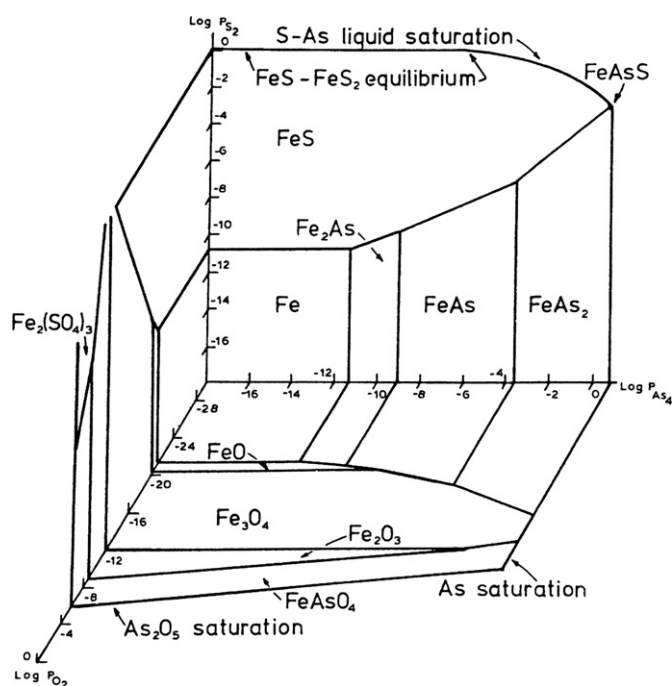
compared to arsenopyrite make the former seem unlikely to be the ore smelted here, even though we cannot rule it out. On balance, we assume that an iron arsenide mineral was smelted – either löllingite ( $\text{FeAs}_2$ ) or arsenopyrite,  $\text{FeAsS}$ .

Löllingite is much rarer than arsenopyrite, and smelting it to produce speiss would only make sense if it was finely dispersed in a gangue or host rock, and needed to be thermally separated from its matrix, i.e. by liquefying the metallic phase. In view of the much more common occurrence of arsenopyrite we assume that this was the starting ore here. Raghavan (1988) reports the sequence of

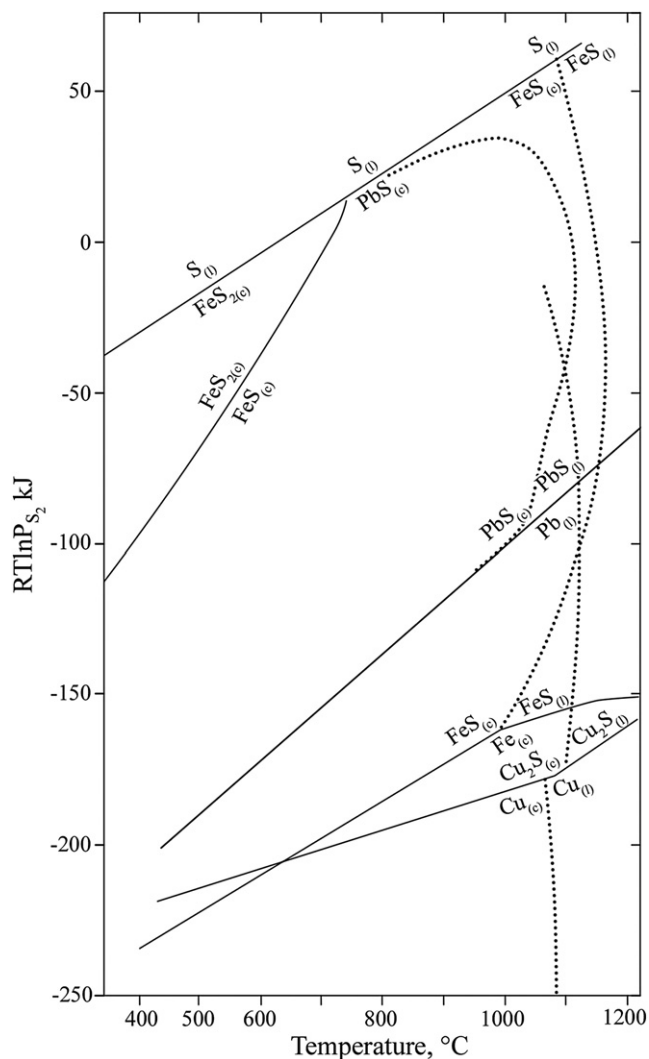
reactions and transformations taking place when heating arsenopyrite up to 1200 °C, and Chakraborti and Lynch (1983) explored the roasting reactions for this mineral. In effect, roasting arsenopyrite – or smelting it under the slightly oxidising conditions recorded here – results in the loss first of the sulphur from the system – depending on circumstances either as sulphur dioxide gas or as a separate iron sulphide-rich melt phase (matte), separate from the iron arsenide melt (speiss). The evidence from the speiss slag shows that some discrete matte prills did form at Arisman, and even more so at Tepe Hissar (Thornton et al., 2009); desulphurization was therefore not complete. Matte and speiss would then separate mechanically from each other and from any slag and metal present, through their mutual immiscibility and different densities in the liquid state (see Fig. 1 in Thornton et al., 2009; based on Keessmann 1991). Oxidising conditions are further indicated by the hot oxidised speiss prills seen in several of the Arisman slags. Thus, we can reasonably assume that these slags formed from the oxidising smelting of arsenopyrite to produce speiss, thereby removing almost all the sulphur from the original ore, probably as sulphur dioxide gas, while also incurring some arsenic loss and forming excess magnetite. Despite its oxidising character and the removal of large amounts of sulphur during the process we prefer to call this ‘smelting’ rather than ‘roasting’, for two main reasons. Firstly, it involves the formation of a fully molten slag, and secondly, it produces a metallic product, speiss, rather than the mixed metal oxides of proper roasting which require further smelting to produce metal. Luyken and Heller (1938) report various roasting experiments in the system Fe–As and Fe–As–Oxide, and noted that under reducing conditions, FeAs is stable up to its melting temperature, while in a  $\text{CO}_2$ -rich atmosphere it reacts to FeO and As vapour, and carbon monoxide. Thus, under the mildly oxidising conditions proposed here arsenic losses would increase significantly once most of the sulphur has been removed from the system.

We argue that it is this removal of the sulphur from the ore which necessitated the smelting in the first place. A recent paper by Willis and Toguri (2009) presenting Ellingham-style diagrams for the reactivity of various metals in relation to sulphur (as opposed to the more common oxygen-based Ellingham diagrams) showed that in a system containing copper, iron, and sulphur at typical furnace temperatures, copper has a higher preference to bond with sulphur than iron (Fig. 10). In contrast, in a system with both metals and oxygen, iron would bond more strongly with the oxygen (see e.g. the traditional Ellingham diagram in Craddock, 1995: 190). Thus, in a system containing both metals, and oxygen and sulphur, it is reasonable to conclude that the iron would form iron oxide which is absorbed into the slag melt, while the copper would preferentially bond with the sulphur to form matte, as a separate melt phase. This, of course, is what also drives the matte smelting in chalcopyrite-based copper metallurgy, and is nothing new in itself.

This process happens regardless of where the various elements originally come from – reacting iron sulphide with copper oxide will invariably form iron oxide and copper sulphide, and adding arsenopyrite to copper metal or copper ore during smelting would result in the sulphur from the arsenopyrite to react with any copper to form copper sulphide, matte (see Fig. 11). Projecting these thermodynamic principles onto EBA copper smelting realities immediately explains why arsenopyrite needed to be smelted to speiss before it could be added to copper metal or copper ore for the production of arsenical copper. During this period, it is reasonable to assume that green, oxidised copper ores were collected for smelting, occasionally including residual sulphidic minerals (Radivojević et al. 2010). Significantly, evidence from the more-or-less contemporary site of Shahr-i Sokhta in the border area between Iran and Afghanistan suggests that at this time, copper matte was considered a waste material and discarded together with the slag



**Fig. 9.** Projection of stability fields of different phases in the system Fe–As–O–S at 973 K and at different partial pressures of oxygen, sulphur and arsenic; adapted from Chakraborti and Lynch (1983).

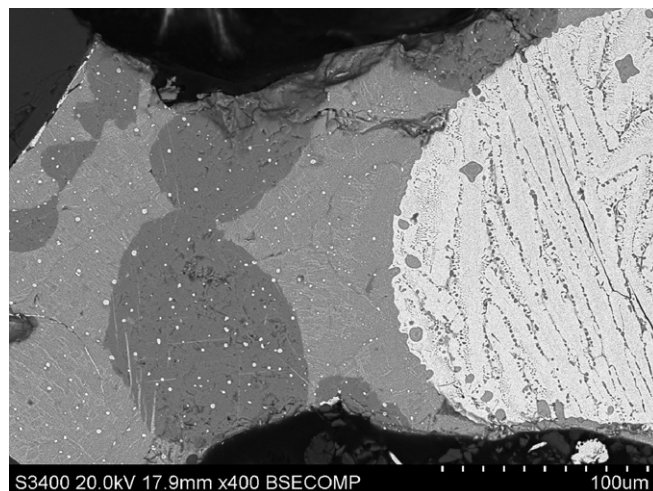


**Fig. 10.** Ellingham-style diagram for iron, copper and lead in relation to sulphur. Redrawn from Willis and Toguri (2009) Figs. 6, 7 and 8. Note that at temperatures above ca. 650 °C, the line for the reaction  $\text{Cu}_2\text{S} - \text{Cu}$  is at lower partial pressures of sulphur than the line  $\text{FeS} - \text{Fe}$ , suggesting that copper reacts preferentially with sulphur compared to iron.

(Hauptmann et al., 2003) – any copper bound as matte would therefore have diminished the metal yield of the smelting operation. Thus, desulphurising arsenopyrite prior to adding it to the smelt as a source of arsenic would have been essential, in particular when smelting an ore already rich in residual sulphidic minerals. The strong and highly diagnostic smells of sulphur dioxide and arsenic oxide, respectively, would have provided an easy clue for the Early Bronze Age smelter when the desulphurisation of the speiss smelt was complete and arsenic losses started – time to stop the smelt and to tap the furnace's content to extract the speiss.

#### 4.2. Smelting arsenical copper

Half of the slag found at Arisman has been identified as copper smelting slag, producing arsenical copper. As noted above, this slag has a substantial amount of copper sulphide prills, reminiscent of the frequent matte prills in LBA copper slags based on chalcopyrite (e.g. Hauptmann, 2007; Pryce et al., 2010). There are several possible scenarios which could explain this. Firstly, the copper ore could have consisted of, or at least contained a substantial amount



**Fig. 11.** SEM-EDS image of iron sulphide (dark grey phase in the center left) preferentially reacting with copper to form matte (grey phase) while a speiss prill (bright phase on the right) remains largely unaffected. Sample FG-030116B.

of copper sulphide minerals such as chalcopyrite. Alternatively, the sulphides might have formed during the reduction of secondary sulphate-bearing copper ore. Thirdly, the sulphur might originate from the addition of a sulph-arsenide mineral such as arsenopyrite. A full discussion of these possibilities is beyond the remit of this paper, even though it is in itself an important question to address; some initial thoughts on this issue are given below. Similarly, at this stage of our research it is unclear whether the arsenic-bearing part of the charge was a natural component of the ore, or whether it had been added intentionally, for instance by using speiss. The slightly higher iron oxide content of the copper slag compared to the speiss slag could be due to the iron in the speiss being oxidised and slagged off. However, the iron oxide might as well originate from the copper ore itself, and we have no pure (i.e. non-arsenical) copper slag from Arisman where we could see what iron oxide 'base line' could be expected from the smelting of such an ore. The observation that metal prills near residual gangue inclusions are virtually pure copper, while those further in the fully reacted slag contain several percent each of arsenic and iron could indicate addition of speiss to the charge. In contrast, the smelting of common secondary copper arsenate minerals, such as olivenite, would produce arsenical copper as soon as a metal phase forms, but not necessarily with such an iron content as observed here.

The production of an iron-rich arsenical copper as seen here does not match the analytical record of EBA arsenical copper objects elsewhere; those have typically much lower iron concentrations, rarely exceeding a quarter of one percent (e.g., Pernicka et al., 1997: 155–156; Begemann et al., 1994: 213). In contrast, the copper prills in the slag from Arisman often have both arsenic and iron in the percentage level. This, however, is no argument against linking Arisman to the production of arsenical copper. Thermodynamic data and experimental observations indicate that arsenic is more noble than iron (Luyken and Heller, 1938: 477), and equilibrium phase diagrams provided by Chakraborti and Lynch (1983) show that re-melting such an alloy under ambient conditions would immediately oxidize the iron ('fire refining'), while the arsenic content would be hardly affected until nearly all of the iron was removed from the alloy. Thus, simple re-casting raw metal rich in arsenic and iron such as the one smelted in Arisman would automatically fire-refine it, resulting in arsenical copper with very low iron content. In fact, even under modern furnace conditions it is difficult to completely remove arsenic from copper by fire refining.



### 4.3. Slag formation

Smelting slag is typically formed from the fusion of gangue components from the ore, the fuel ash, absorbed ceramic from the furnace structure, some metal oxide that did not reduce to metal, and flux (if any). Identifying the various contributing components and their relative proportions within a slag assemblage is essential for a more detailed understanding of the metallurgical processes that led to the formation of this slag, of the nature of the raw materials used, and of technical choices taken by the ancient smelters. However, assigning specific oxides to their raw materials of origin is not a trivial task, since most oxides in the slag can come from more than one of the potential raw materials. This makes proper mass balance calculations difficult, as the starting compositions of most raw materials are unknown. This is the case here, too, where only the technical ceramic is relatively reliably known in its composition, and accordingly only a tentative discussion of the contribution from the other raw materials is possible.

The composition of the slags from Arisman is characterised by relatively high lime content (15% CaO) and low iron oxide (~15–25% FeO) compared to other copper slags. We commented earlier that the slag compositions are unusually close to the composition of the technical ceramic, which might suggest that the technical ceramic contributed greatly to the slag formation. For the following discussion we assume that the only source for alumina in the slag is the technical ceramic, while all other components could originate from multiple sources. This is borne out by the fact that in the slag all other oxides are enriched relative to alumina, and at different degrees. Table 7 gives the average concentrations of the main oxides for the technical ceramic, grey and brown slag, with alumina, silica, lime and iron oxide adding up to around 90% of the total compositions. The apparent drop in alumina content in the slag compared to the ceramic suggests that the slag consists to about 60% of fused ceramic, with 40% being from additional materials. Of these, fuel ash is likely to account for the slight increase in lime in the slags relative to the ceramic, and possibly also for some of the additional silica (for wood ash analyses, see Stern and Gerber, 2004; Jackson and Smedley, 2008; or Wood, 2009; and references therein). The bulk of additional material, however, is iron oxide, accounting for about 2/3 of the composition not explained by the ceramic contribution.

This is true for both the grey copper slag and the brown speiss slag, but this does not necessarily mean that these formed from smelting the same ore. We argued above that the brown slag formed from smelting arsenopyrite, FeAsS, to form speiss, basically FeAs. Nominally, this could be achieved by a simple loss of sulphur, with no iron entering into the slag. However, it seems likely from our data that this reaction involved a great deal of iron to oxidise and enter into the slag. This could either indicate that an equivalent amount of arsenic was lost as vapour (metallic or as oxide), or the arsenopyrite mineral was intergrown in the ore with pyrite or marcasite, both common iron sulphides regularly associated with arsenopyrite. This arsenopyrite ore may also have contained some quartz as gangue, contributing to the higher silica to alumina ratio of the slag relative to the ceramic.

For the grey copper slag, we postulate an origin from the smelting of a 'green' secondary copper ore to produce arsenical

copper. The resulting slag is again consistent with its majority originating from the ceramic and some fuel ash, and a significant amount of additional iron oxide. Here, two scenarios are equally able to explain our data. One possibility is that a complex ore containing the oxides (or carbonates) of copper, arsenic and iron was smelted to produce arsenical copper as a natural alloy. Alternatively, the ancient smelters could have added some of the speiss produced separately to the copper ore, with the intention to producing arsenical copper. The additional iron oxide in the slag could then originate partly from the copper ore and partly from the speiss, following preferential uptake of arsenic into the copper metal and partial oxidation of the iron from the speiss. However, the high average iron content in the arsenical copper prills suggests that most of the assumed added speiss was absorbed completely by the metallic copper, as one would expect to happen under the reducing conditions of copper smelting.

Chemically, the bulk composition of the grey copper slag is equally well explained by either of these scenarios, and both appear possible in the context of a developed Early Bronze Age metallurgy in Iran. The only indication favouring one scenario over the other is the microanalytical observation in two of the grey slag samples that copper prills near residual gangue material (chiefly quartz) are very low in iron and almost free of arsenic, while prills in the same samples but away from the gangue remains and embedded in fully molten slag are invariably rich in both arsenic and iron (see Table 2). To us, this suggests that the scenario of added speiss to a low-arsenic secondary copper ore, intergrown with some iron hydroxides, is the more likely of the two. However, further detailed study of more such samples is necessary to explore this issue further.

The strong contribution to the slag from fused ceramic material, possibly exceeding half of the total slag weight, is indicative of the use of a very low-refractory furnace material and associated major ceramic erosion during use, possibly related to the processing of ores which are low in slag-forming gangue materials, that is rich in metal-bearing minerals. If the latter were indeed true, then the amount of slag present at Area A in Arisman would point to a rather substantial production of metal, of the order of multiples of the weight of slag produced.

### 4.4. Slag morphology

Above, we have described the slag variously as being 'pasty' in appearance as well as having clear features of tap slags; also, we report that both 'hot' contact between the slag and furnace wall material occurred and 'cold' contact of slag which looks as if it was being manipulated on a flat ceramic surface just before it solidified. Additional evidence exists for the tapping of slag together with a denser fluid (matte, speiss or metal) into ceramic receptacles, akin to observations from the contemporary workshops at Shahr-i Sokhta (Hauptmann et al., 2003; see their Fig. 2 and our Fig. 12). Little evidence though exists for a regular crushing of the slag at Arisman to mechanically retrieve metal prills trapped in it, an activity common in European and Levantine early copper metallurgy (see e.g. Bachmann, 1980, 1982: 108–110: 21–22, Betancourt, 2006: 187). These manipulations of semi-liquid slag are also known from sulphide-based EBA copper smelting in Anatolia (Rehren and Radivojević 2010), and certainly were done to improve the separation of metal from slag; future research will have to study the shape of a larger number of slags and ceramic fragments in more detail to better understand the mechanics of this process. What seems clear, though, is that at this stage in the metallurgical development slag and metal were tapped together from the furnace, as opposed to the selective tapping of slag and metal common for later metallurgy.

**Table 7**

Main oxide bulk composition averages for the technical ceramics and slags. Data in wt%.

	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	FeO	Total
Technical ceramics	13	53	17	6	89
Brown slag	9	42	16	24	91
Grey slag	8	43	13	27	91

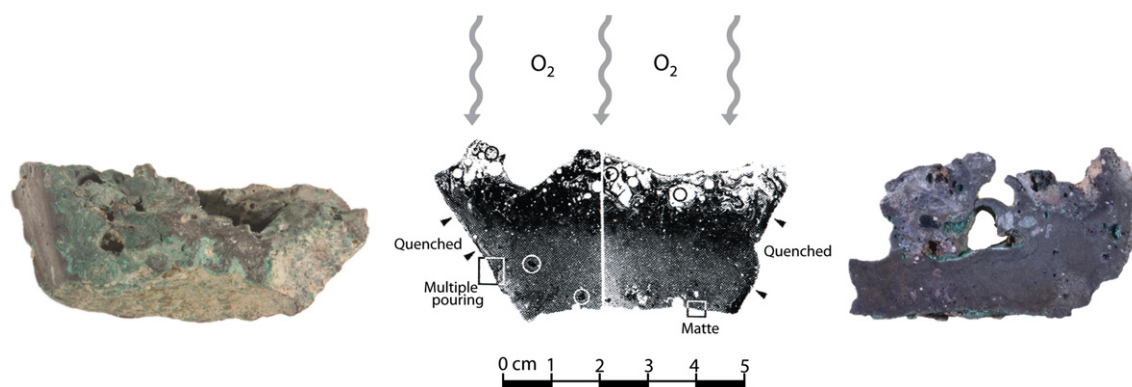


Fig. 12. Plate showing the similarity in shape between some Arisman copper slags (far right) and Shahr-i Sokhta tapped copper slags (far left). The center image is a photodiagram from Hauptmann et al. (2003), Fig. 2, p 201.

## 5. Conclusion and outlook

The investigation of different slag types from the large Early Bronze Age slag heap Area A at Arisman, estimated to contain some 20 tons of slag, revealed that both arsenical copper and speiss were smelted here. We argue that the copper source was a secondary, 'green' ore while the speiss was most likely smelted from an ore rich in arsenopyrite. The speiss would have been intended as a source of arsenic to produce arsenical copper – either by adding it to an oxidic copper ore during smelting, or later in an alloying operation with separately smelted copper metal. The smelting of arsenopyrite was necessary to remove its sulphur content, and therefore took place under more oxidising conditions than those typical of copper smelting. Any residual sulphur still present in this charge, either from incompletely weathered primary copper minerals or from minor amounts of sulphur preserved in the speiss, led to the formation of copper matte, which may have been considered a waste material – in analogy to the evidence from Shahr-i Sokhta. The arsenical copper thus produced was relatively rich in iron; analyses of metal prills from the grey slag indicate almost equal levels of arsenic and iron in the copper, of around three to five weight percent. A simple re-melting operation under oxidising conditions, such as melting prior to casting, would have selectively oxidised the iron content, but not the arsenic, giving an alloy similar in composition to that found frequently in EBA artefacts.

The bulk of the slag at Area A is either grey or brown. However, several other types of metallurgical waste were also found, in addition to the copper slag and speiss slag described above. There are more glassy-black slags, containing inclusions of arsenical copper, matte and speiss, and with an iron oxide content much nearer to the fused ceramic; it is unclear at present whether these are related to the re-melting of arsenical copper, transferring the excess iron as iron oxide into the slag, or whether they simply reflect the initial variability in iron oxide content of the copper ore, and are part of a broader continuum incorporating both grey and black slags. It is hoped that a more extensive study of this material can shed light on this issue, and also on the significance of other metallurgical waste, such as lead slag and litharge found at other slag heaps at Arisman.

Another question requiring further research concerns the possible use of speiss as a commodity for export. Thornton et al. (2009) give an overview of the occurrence of speiss in EBA copper workshops; it may suffice here to mention that it was found as far west as Crete (misidentified as löllingite mineral in Doonan et al., 2007), suggesting that speiss may have been an important item of long-distance trade, and therefore likely to have been

included in economic or trade correspondence. Clearly, more research is necessary, in the field, in the laboratory and the library before we more fully understand the real levels of Early Bronze Age metallurgical sophistication achieved at sites such as Arisman.

## Acknowledgements

This manuscript is based on research done as part of Loïc Boscher's MSc in Technology and Analysis of Archaeological Materials at the UCL Institute of Archaeology, under the umbrella of Ernst Pernicka's investigation of the metallurgical remains from Arisman, excavated by the Deutsches Archäologisches Institut under the direction of Barbara Helwing. Her support and permission to analyse the material, and funding from the Deutsche Forschungsgemeinschaft for the Arisman project, are greatly appreciated. We are grateful for Simon Groom and Kevin Reeves for their support in the laboratory, and their patience. The Iranian Authorities are thanked for permitting the export of the samples for analysis, and the excavation licence. We benefited from discussions with Peter Northover (Oxford), David Killick (Tucson) and Hadi Özbal (Istanbul) about early arsenic metallurgy, and the comments from two anonymous reviewers; any remaining errors are ours.

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